

New Investigations of Cytosine and Its Monohydrate

BY R. J. MCCLURE AND B. M. CRAVEN

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pa 15260, U.S.A.

(Received 20 November 1972; accepted 30 January 1973)

Cytosine is orthorhombic, space group $P2_12_12_1$, with $a = 13.044$ (2), $b = 9.496$ (1), $c = 3.814$ (1) Å, $Z = 4$. Cytosine monohydrate is monoclinic, space group $P2_1/c$, with $a = 7.783$ (2), $b = 9.825$ (2), $c = 7.668$ (2) Å, $\beta = 99^\circ 34$ (1)', $Z = 4$. The bond lengths of the carbonyl group, previously reported to be different in cytosine and the monohydrate, are presently found to be 1.241 and 1.251 Å, respectively. This and other differences in molecular structure are of marginal significance.

Introduction

The crystal structures of cytosine (Barker & Marsh, 1964; hereafter BM) and its monohydrate (Jeffrey & Kinoshita, 1963; hereafter JK) have been determined from photographic intensity data. It was found that the carbonyl bond length was significantly longer (1.260 *vs.* 1.234 Å) in the monohydrate. This difference was attributed to the effect of hydrogen bonding. Similar but smaller (0.01 Å) effects have been reported in a series of barbiturate crystal structures (Craven, Cusatis, Gartland & Vizzini, 1973). Barbiturate bond length differences are associated with greater hydrogen bonding differences than are found in cytosine and its monohydrate. We have redetermined the latter structures in an attempt to resolve this inconsistency.

Experimental

Crystals of cytosine and its monohydrate were obtained as described by BM and JK. The crystal of cytosine which was selected for data collection measured 0.3 × 0.3 × 0.6 mm and was mounted in an arbitrarily chosen orientation, with the longest crystal dimension (c^*) approximately 20° from the diffractometer φ axis. The monohydrate crystal measured 0.2 × 0.2 × 0.5 mm

and was mounted with the longest dimension (b^*) approximately 19° from the diffractometer φ axis. The X-ray data were measured using a computer controlled four-circle diffractometer with nickel-filtered Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). The lattice parameters are in good agreement with those of BM but are smaller than those of JK by about 0.02 Å, possibly because the latter did not take film shrinkage into account.

Intensity data were collected in the asymmetric region of reciprocal space with $2\theta_{\max} = 130^\circ$ using $\theta/2\theta$ scans at 30 sec deg^{-1} 2θ and with background counts of 10 sec at each scan limit. In the case of the monohydrate, the use of a smaller crystal gave a higher proportion of unobservably weak reflections. For this reason, a second data set was measured, using the same scan rate but with 20 sec background counts. The two sets were averaged with equal weights for integrated intensities greater than 1.5 $\sigma(I)$. Data collection was monitored by the use of three standard reflections which exhibited no significant intensity changes. No corrections were made for X-ray absorption or extinction. Integrated intensities less than 1.5 $\sigma(I)$ were considered to be unobservably weak and were assigned values of $\sigma(I)$.

The atomic parameters of BM and JK were refined by a full-matrix least-squares procedure. The function $\sum w(\Delta F)^2$ was minimized, using the weights given in

Table 1. *Intensity data and refinement criteria*

	Anhydrous	Monohydrate
Number of intensity data:		
(a) Observed	431	749
(b) Unobservably weak	74	129
Weighting scheme, $w(F) = 1/\sigma^2(F)$		
$\sigma^2(F) = A + BF + CF^2$		
<i>A</i>	0.231	0.185
<i>B</i>	-0.535	-0.400
<i>C</i>	0.0036	0.00325
Standard deviation of observation of unit weight	1.18	1.03
<i>R</i> index,* including unobserved reflections	0.039	0.047
<i>R</i> index, excluding unobserved reflections	0.031	0.037
Weighted <i>R</i> index, including unobserved reflections	0.040	0.051
Weighted <i>R</i> index, excluding unobserved reflections	0.034	0.045

$$* R = \frac{\sum_h |\Delta F|}{\sum_h |F_{\text{meas}}|} \text{ where } \Delta F = |F_{\text{meas}}| - |F_{\text{calc}}|.$$

Table 2. Observed and calculated structure factors

Successive columns contain h , $10|F_{\text{obs}}|$ and $10F_{\text{calc}}$. Reflections marked with an asterisk were unobservably weak.

(a) Anhydrous cytosine

10	0	0	10	74	76	112	38	50	9	119	9	122	2	2	14	32	37	1	14	22	9	45	46	2	55	55	4	220	233	8	58	52	0	90	87	1	42	41	3	37	40	1	26	28	2	27	27
2	10	0	2	137	137	12	47	48	1	150	150	10	22	22	1	14	14	1	14	22	9	45	46	2	55	55	4	220	233	8	58	52	0	90	87	1	42	41	3	37	40	1	26	28	2	27	27
3	20	0	3	264	264	24	94	95	2	300	300	20	44	44	2	28	28	2	28	44	20	110	110	6	110	110	8	440	466	16	116	116	0	180	177	2	84	83	5	74	74	5	52	54	5	52	53
4	30	0	4	391	391	36	141	142	3	450	450	30	66	66	3	42	42	3	42	66	30	165	165	12	165	165	12	660	699	24	174	174	0	270	267	7	126	125	10	102	102	7	78	79	10	78	79
5	40	0	5	518	518	48	187	188	4	600	600	40	88	88	4	56	56	4	56	88	40	220	220	16	220	220	16	880	932	32	232	232	0	360	357	14	168	168	14	136	136	14	136	137	14	136	137
6	50	0	6	645	645	60	254	255	5	750	750	50	110	110	5	74	74	5	74	110	50	330	330	24	330	330	24	1100	1164	48	312	312	0	480	477	21	240	240	21	240	241	21	240	241			
7	60	0	7	772	772	72	341	342	6	900	900	60	152	152	6	104	104	6	104	152	60	440	440	32	440	440	32	1520	1596	64	392	392	0	580	577	28	320	320	28	320	321	28	320	321			
8	70	0	8	900	900	84	432	433	7	1050	1050	70	194	194	7	126	126	7	126	194	70	560	560	40	560	560	40	1940	2016	80	496	496	0	700	697	35	400	400	35	400	401	35	400	401			
9	80	0	9	1028	1028	96	524	525	8	1200	1200	80	236	236	8	158	158	8	158	236	80	680	680	48	680	680	48	2360	2448	96	592	592	0	840	837	42	480	480	42	480	481	42	480	481			
10	90	0	10	1156	1156	108	616	617	9	1350	1350	90	278	278	9	190	190	9	190	278	90	820	820	56	820	820	56	2780	2880	112	696	696	0	980	977	46	560	560	46	560	561	46	560	561			
11	100	0	11	1284	1284	120	708	709	10	1500	1500	100	320	320	10	222	222	10	222	320	100	960	960	64	960	960	64	3200	3312	128	808	808	0	1140	1137	50	640	640	50	640	641	50	640	641			
12	110	0	12	1412	1412	132	800	801	11	1650	1650	110	362	362	11	264	264	11	264	362	110	1120	1120	72	1120	1120	72	3620	3744	156	904	904	0	1300	1297	54	720	720	54	720	721	54	720	721			
13	120	0	13	1540	1540	144	892	893	12	1800	1800	120	404	404	12	306	306	12	306	404	120	1280	1280	80	1280	1280	80	4040	4176	172	992	992	0	1460	1457	58	800	800	58	800	801	58	800	801			
14	130	0	14	1668	1668	156	984	985	13	1950	1950	130	446	446	13	348	348	13	348	446	130	1460	1460	88	1460	1460	88	4460	4648	184	1080	1080	0	1600	1597	60	880	880	60	880	881	60	880	881			
15	140	0	15	1796	1796	168	1076	1077	14	2100	2100	140	488	488	14	390	390	14	390	488	140	1600	1600	96	1600	1600	96	4880	5088	192	1168	1168	0	1740	1737	62	960	960	62	960	961	62	960	961			
16	150	0	16	1924	1924	180	1168	1169	15	2250	2250	150	530	530	15	432	432	15	432	530	150	1700	1700	104	1700	1700	104	5300	5512	208	1256	1256	0	1880	1877	64	1040	1040	64	1040	1041	64	1040	1041			
17	160	0	17	2052	2052	192	1260	1261	16	2400	2400	160	572	572	16	474	474	16	474	572	160	1800	1800	112	1800	1800	112	5720	5944	216	1344	1344	0	2020	2017	66	1120	1120	66	1120	1121	66	1120	1121			
18	170	0	18	2180	2180	204	1352	1353	17	2550	2550	170	614	614	17	516	516	17	516	614	170	1900	1900	120	1900	1900	120	6140	6376	224	1432	1432	0	2160	2157	68	1200	1200	68	1200	1201	68	1200	1201			
19	180	0	19	2308	2308	216	1444	1445	18	2700	2700	180	656	656	18	558	558	18	558	656	180	2000	2000	128	2000	2000	128	6560	6816	232	1520	1520	0	2300	2297	70	1280	1280	70	1280	1281	70	1280	1281			
20	190	0	20	2436	2436	232	1536	1537	19	2850	2850	190	698	698	19	600	600	19	600	698	190	2100	2100	136	2100	2100	136	6980	7248	240	1608	1608	0	2400	2397	72	1360	1360	72	1360	1361	72	1360	1361			
21	200	0	21	2564	2564	248	1628	1629	20	3000	3000	200	740	740	20	642	642	20	642	740	200	2200	2200	144	2200	2200	144	7400	7664	248	1696	1696	0	2500	2497	74	1440	1440	74	1440	1441	74	1440	1441			
22	210	0	22	2692	2692	264	1720	1721	21	3150	3150	210	782	782	21	684	684	21	684	782	210	2300	2300	152	2300	2300	152	7820	8088	256	1784	1784	0	2600	2597	76	1520	1520	76	1520	1521	76	1520	1521			
23	220	0	23	2820	2820	280	1812	1813	22	3300	3300	220	824	824	22	726	726	22	726	824	220	2400	2400	160	2400	2400	160	8240	8512	264	1872	1872	0	2700	2697	78	1600	1600	78	1600	1601	78	1600	1601			
24	230	0	24	2948	2948	296	1904	1905	23	3450	3450	230	866	866	23	768	768	23	768	866	230	2500	2500	168	2500	2500	168	8660	8936	272	1960	1960	0	2800	2797	80	1680	1680	80	1680	1681	80	1680	1681			
25	240	0	25	3076	3076	308	1996	1997	24	3600	3600	240	908	908	24	810	810	24	810	908	240	2600	2600	176	2600	2600	176	9080	9360	280	2048	2048	0	2900	2897	82	1760	1760	82	1760	1761	82	1760	1761			
26	250	0	26	3204	3204	316	2088	2089	25	3750	3750	250	950	950	25	852	852	25	852	950	250	2700	2700	184	2700	2700	184	9500	9784	288	2136	2136	0	3000	2997	84	1840	1840	84	1840	1841	84	1840	1841			
27	260	0	27	3332	3332	328	2180	2181	26	3900	3900	260	992	992	26	894	894	26	894	992	260	2800	2800	192	2800	2800	192	9920	10208	296	2224	2224	0	3100	3097	86	1920	1920	86	1920	1921	86	1920	1921			
28	270	0	28	3460	3460	340	2272	2273	27	4050	4050	270	1034	1034	27	936	936	27	936	1034	270	2900	2900	200	2900	2900	200	10340	10632	304	2312	2312	0	3200	3197	88	2000	2000	88	2000	2001	88	2000	2001			
29	280	0	29	3588	3588	352	2364	2365	28	4200	4200	280	1076	1076	28	978	978	28	978	1076	280	3000	3000	208	3000	3000	208	10760	11064	312	2400	2400	0	3300	3297	90	2080	2080	90	2080	2081	90	2080	2081			
30	290	0	30	3716	3716	364	2456	2457	29	4350	4350	290	1118	1118	29	1020	1020	29	1020	1118	290	3100	3100	216	3100	3100	216	11180	11472	320	2488	2488	0	3400	3397	92	2160	2160	92	2160	2161	92	2160	2161			
31	300	0	31	3844	3844	376	2548	2549	30	4500	4500	300	1160	1160	30	1062	1062	30	1062	1160	300	3200	3200	224	3200	3200	224	11600	11904	328	2576	2576	0	3500	3497	94	2240	2240	94	2240	2241	94	2240	2241			
32	310	0	32	3972	3972	388	2640	2641	31	4650	4650	310	1202	1202	31	1104	1104	31	1104	1202	310	3300	3300	232	3300	3300	232	12020	12312	336	2664	2664	0	3600	3597	96	2320	2320	96	2320	2321	96	2320	2321			
33	320	0	33	4100	4100	400	2732	2733	32	4800	4800	320	1244	1244	32	1146	1146	32	1146	1244	320	3400	3400	240	3400	3400	240	12440	12736	344	2752	2752	0	3700	3697	98	2400	2400	98	2400	2401	98	2400				

Table 3 (cont.)

(b) Hydrogen atoms

	x	y	z
H(1)	-0.013 (2)	-0.057 (3)	0.363 (7)
	0.031 (2)	-0.067 (2)	0.236 (2)
H(3)	0.154 (2)	0.463 (3)	0.541 (9)
	0.259 (3)	0.434 (2)	0.157 (2)
H(4)	0.248 (2)	0.378 (2)	0.652 (8)
	0.408 (3)	0.361 (2)	0.098 (3)
H(5)	0.237 (2)	0.128 (2)	0.796 (8)
	0.420 (3)	0.122 (2)	0.087 (3)
H(6)	0.132 (2)	-0.078 (3)	0.692 (8)
	0.285 (2)	-0.086 (2)	0.148 (2)
HW(1)	—	—	—
	-0.294 (3)	0.250 (2)	0.105 (3)
HW(2)	—	—	—
	-0.285 (3)	0.323 (2)	-0.039 (3)

Table 1. Atomic scattering factors for carbon, nitrogen and oxygen from *International Tables for X-ray Crystallography* (1962) were used. The values of Stewart, Davidson & Simpson (1965) were used for hydrogen atoms. Thermal parameters for each hydrogen atom were assumed to be the same as the atom to which it is bonded. The refinement converged satisfactorily (Table 1).

Observed and calculated structure amplitudes are given in Table 2 and atomic parameters in Table 3. The anisotropic thermal parameters were analyzed in terms of the rigid-body model (Schomaker & Trueblood, 1968). A comparison of experimental (U_{meas}) and calculated (U_{calc}) anisotropic atomic thermal parameters shows that the assumed rigid-body vibration is a fair approximation, particularly for the anhydrous crystal structure. Thus the values of $[\sum(U_{meas} - U_{calc})^2/(n-s)]^{1/2}$ are 0.0014 \AA^2 for the anhydrous and 0.0017 \AA^2 for the monohydrate structures. For the anhydrous crystal structure there are 8 U_{ij} values out of 48 for which $|U_{meas} - U_{calc}|/\sigma(U_{meas})$ exceeds 2. The corresponding number is 19 for the monohydrate. The poorest agreement (4.2σ) is in U_{22} for the atom N(4) in the monohydrate. The librational tensor components for the cytosine molecule in the two crystal structures are very similar when they are compared with respect to the same molecular axial system (Table 4). The greatest

difference in the resulting bond length corrections is for C(6)-N(1), the values being 0.004 \AA in anhydrous cytosine and 0.006 \AA in the monohydrate. The corrections

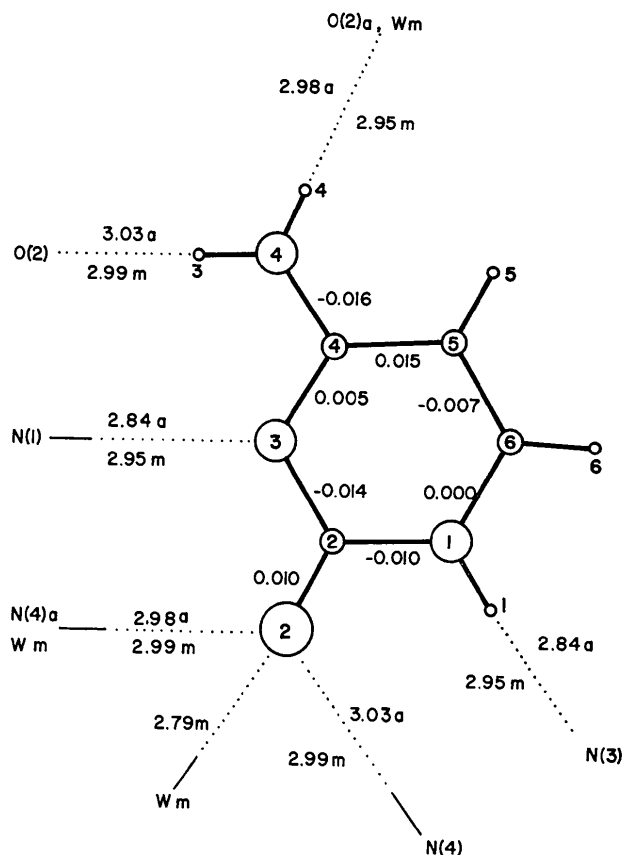


Fig. 1. Comparison of cytosine in the anhydrous and monohydrated crystal structures. Circles of decreasing size represent oxygen, nitrogen, carbon and hydrogen atoms. Atomic numbering is consistent with Table 3. Numbers alongside the C-O, C-N and C-C bonds are the bond length difference (monohydrate-anhydrous) in \AA . The hydrogen bonding environment of the cytosine molecule in both structures is represented schematically. Atom labels and N...O or N...N hydrogen bond lengths are followed by a or m denoting anhydrous or monohydrate respectively. Atoms not labeled in this way are the same in both crystal structures.

Table 4. Rigid-body thermal motion analysis

The tensors L for libration, T for translation and S for screw motion are referred to an origin at the molecular centroid with fractional coordinates (0.0681, 0.1771, 0.469) and (0.1402, 0.1547, 0.1905) in the anhydrous and monohydrate structures respectively. Tensor components are with respect to an orthogonal molecular axial system with axis (1) the normal to the molecular plane, axis (2) along the vector C(6) \rightarrow N(3), and axis (3) completing a right-handed system.

	Cytosine	Cytosine monohydrate
$L, \sigma(L)$ (degrees ²)	$\begin{bmatrix} 5.7 (1.6) & -1.5 (1.6) & -2.0 (1.8) \\ -1.5 & 12.6 (1.7) & 2.4 (1.8) \\ -2.0 & 2.4 & 20.4 (2.2) \end{bmatrix}$	$\begin{bmatrix} 5.6 (1.6) & -0.2 (1.8) & 1.2 (2.1) \\ -0.2 & 16.9 (2.1) & 5.1 (2.3) \\ 1.2 & 5.1 & 22.6 (2.9) \end{bmatrix}$
(L_1, L_2, L_3)	(21.5 12.2 5.3)	(24.7 16.8 5.6)
$T, \sigma(T)$ (\AA^2)	$\begin{bmatrix} 0.0238 (12) & 0.0023 (8) & 0.0026 (9) \\ 0.0023 & 0.0237 (8) & 0.0005 (8) \\ 0.0026 & 0.0005 & 0.0265 (8) \end{bmatrix}$	$\begin{bmatrix} 0.0315 (15) & 0.0005 (10) & 0.0019 (11) \\ 0.0005 & 0.0223 (9) & 0.0008 (9) \\ 0.0019 & 0.0008 & 0.0257 (9) \end{bmatrix}$
T_1, T_2, T_3	(0.029 0.024 0.021)	(0.032 0.026 0.022)
S , (degree \AA)	$\begin{bmatrix} -0.01 & -0.04 & 0.09 \\ 0.01 & -0.04 & -0.05 \\ 0.08 & -0.03 & 0.05 \end{bmatrix}$	$\begin{bmatrix} 0.00 & 0.01 & 0.05 \\ 0.02 & 0.00 & -0.01 \\ 0.03 & -0.02 & 0.00 \end{bmatrix}$

for the bond length C(2)–O(2) are 0.004 and 0.005 Å, respectively.

Discussion

We have chosen an atomic numbering system which is different from those of BM and JK, but which is more consistent with chemical usage (Fig. 1). Bond lengths and angles for the cytosine molecule are listed in Table 5, together with the values reported by BM and JK. Our values for the water molecule in cytosine are 0.84 and 0.82 Å for the O–H bond lengths and 106° for the H–O–H angle.

The differences in bond lengths of cytosine in the anhydrous and monohydrate crystal structures are shown in Fig. 1. The largest difference (0.016 Å), which is in the bond length C(4)–N(4) is significant (3.5 σ) in terms of the e.s.d.'s derived from the least-squares refinement. However, these are probably underestimated, and it is unlikely that any of the bond length differences, including that of C(2)–O(2) (0.010 Å), are more than possibly significant.

Although the crystal structures of cytosine and its monohydrate are quite different. Fig. 1 shows that the hydrogen bonding interactions of the cytosine molecule are similar, particularly at atom N(4). The N(1)H \cdots N(3) hydrogen bond is stronger in the anhydrous crystal structure, as shown by the shorter N(1) \cdots N(3) distance (2.84, 2.95 Å). Of the hydrogen bonds formed at O(2), the N(4)H(3) \cdots O distances are similar (3.03, 2.99 Å). The N(4)H(4) \cdots O distance (2.98 Å) in the anhydrous structure and the corresponding O–H \cdots O distance (2.79 Å) in the monohydrate are both about 0.1 Å longer than the distance corresponding to the peak in the observed distribution of hydrogen bonded N \cdots O and O \cdots O distances (Pimentel & McClellan, 1959; Voet & Rich, 1970). The greatest difference thus lies in the second OH–O hydrogen bond in the monohydrate. This is a very weak interaction (O \cdots O distance 2.99 Å), but it has no counterpart in the anhydrous structure.

Thus, bond length differences which might be attributed to hydrogen bonding effects in cytosine and

Table 5 *Bond lengths and angles*

These parameters are not corrected for the effect of thermal motion.

	Cytosine		Cytosine monohydrate	
	BM $\sigma=0.003$ Å	Present study $\sigma=0.003$ Å	JK $\sigma=0.004$ Å	Present study $\sigma=0.002$ Å
N(1)–C(2)	1.374 Å	1.381 Å	1.376 Å	1.371 Å
C(2)–N(3)	1.364	1.364	1.354	1.350
N(3)–C(4)	1.337	1.336	1.351	1.341
C(4)–C(5)	1.424	1.410	1.432	1.425
C(5)–C(6)	1.342	1.340	1.348	1.333
C(6)–N(1)	1.357	1.353	1.361	1.353
C(2)–O(2)	1.234	1.241	1.260	1.251
C(4)–N(4)	1.330	1.342	1.332	1.326
	$\sigma=0.04$ Å	$\sigma=0.03$ Å	—	$\sigma=0.02$ Å
N(1)–H(1)	0.88 Å	0.98 Å	0.87 Å	0.86 Å
N(4)–H(3)	0.87	0.89	0.89	0.85
N(4)–H(4)	0.86	0.86	0.83	0.84
C(5)–H(5)	0.87	0.99	0.85	0.89
C(6)–H(6)	1.01	1.01	0.87	0.97
	$\sigma=0.2^\circ$	$\sigma=0.2^\circ$	$\sigma=0.4^\circ$	$\sigma=0.15^\circ$
C(2)–N(1)–C(6)	122.7°	121.9°	121.3°	121.5°
N(3)–C(2)–N(1)	118.1	118.2	120.1	119.6
C(2)–N(3)–C(4)	119.9	119.4	118.9	119.1
N(3)–C(4)–C(5)	122.0	122.7	122.0	121.7
C(4)–C(5)–C(6)	117.3	117.0	117.1	117.5
C(5)–C(6)–N(1)	120.1	120.8	120.6	120.5
N(1)–C(2)–O(2)	119.8	119.5	118.4	118.5
N(3)–C(2)–O(2)	122.2	122.2	121.5	121.9
N(3)–C(4)–N(4)	118.2	117.1	117.8	118.1
C(5)–C(4)–N(4)	119.9	120.2	120.2	120.2
	$\sigma=2^\circ$	$\sigma=2^\circ$	—	$\sigma=1.4^\circ$
C(2)–N(1)–H(1)	120°	117°	116°	118°
C(6)–N(1)–H(1)	117	120	123	121
C(4)–N(4)–H(3)	123	120	119	117
C(4)–N(4)–H(4)	124	117	118	118
H(3)–N(4)–H(4)	114	123	122	124
C(4)–C(5)–H(5)	123	121	126	120
C(6)–C(5)–H(5)	119	122	117	123
C(5)–C(6)–H(6)	122	124	123	125
N(1)–C(6)–H(6)	118	115	116	114

cytosine monohydrate should be of marginal significance, in agreement with our findings.

This work was supported by Grant Nos. NS-02763 and GM-01728 of the U.S. Public Health Service, National Institutes of Health. The IBM 1130 and 7090 computer programs used were those written or modified by Dr R. Shiono and J. Rutherford.

References

BARKER, D. L. & MARSH, R. E. (1964). *Acta Cryst.* **17**, 1581–1587.

CRAVEN, B. M., CUSATIS, C., GARTLAND, G. L. & VIZZINI, E. A. (1973). *J. Mol. Struct.* In the press.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 JEFFREY, G. A. & KINOSHITA, Y. (1963). *Acta Cryst.* **16**, 20–38.
 PIMENTEL, G. C. & MCCLELLAN, A. L. (1959). *The Hydrogen Bond*. San Francisco: Freeman.
 SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 VOET, D. & RICH, A. (1970). *Prog. Nucleic Acid Res. Mol. Biol.* **10**, 183–264.

Acta Cryst. (1973). **B29**, 1238

The Crystal Structure of Naphtho[b]cyclobutene*

BY JAMES L. CRAWFORD† AND RICHARD E. MARSH

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109, U.S.A.

(Received 28 December 1972; accepted 5 February 1973)

Crystals of naphtho[b]cyclobutene, $C_{12}H_{10}$, are monoclinic, space group $P2_1/c$, with $a = 5.796$ (2), $b = 18.015$ (8), $c = 8.291$ (3) Å, $\beta = 106.50$ (3)°. A structure determination, based on 1228 reflections measured on a diffractometer, led to an R index of 0.035 and estimated deviations of about 0.0015 Å in the coordinates of the C atoms and 0.015 Å in the coordinates of the H atoms. The fusion of the cyclobutene ring results in small distortions in the naphthalene grouping, presumably due to bond-angle constraints at C(2) and C(3).

Introduction

This work is part of a program of studies on the geometries of strained fused-ring compounds.

Experimental

Crystals of naphtho[b]cyclobutene, which was first synthesized by Cava & Shirley (1960), were supplied by Dr Ashley Cooper of the Jet Propulsion Laboratory, Pasadena. They were colorless prisms, somewhat elongated along **a**. They sublime slowly at room temperature. The crystal used in this work had dimensions $0.36 \times 0.30 \times 0.30$ mm (along **a**, **b** and **c**) and was sealed in a 0.3 mm diameter thin-walled glass capillary to prevent sublimation. Preliminary rotation and Weissenberg photographs showed monoclinic symmetry with systematic absences ($h0l$, l odd; $0k0$, k odd) characteristic of space group $P2_1/c$. The crystal was then mounted on a General Electric quarter-circle diffractometer, automated by Datex and highly modified

by Dr Sten Samson. Cell dimensions were obtained from a least-squares fit to 2θ values for 15 reflections; they are given in Table 1. We did not measure the crystal density.

Table 1. *Crystal data*

Naphtho[b]cyclobutene	$C_{12}H_{10}$
Monoclinic	F.W. 154.2
Space group, $P2_1/c$	m.p. 86°C*
$a = 5.796$ (2) Å	$Z = 4$
$b = 18.015$ (8)	$F(000) = 328$
$c = 8.291$ (3)	$D_x = 1.23$ g cm ⁻³
$\beta = 106.50$ (3)°	$\mu = 4$ cm ⁻¹
$V = 830.1$ (9) Å ³	$\lambda(\text{Cu } K\alpha) = 1.5418$ Å

* Cava & Shirley (1960).

Intensities were measured using Cu $K\alpha$ radiation and θ - 2θ scans at a speed of 2° (in 2θ) per min; backgrounds were counted for 30 sec at the extrema. The $11\bar{2}$ reflection was monitored every 20 reflections; its intensity decreased from 864,000 to 820,000 counts – about 5% – during the one-week period of data collection. All reflections in one quadrant of reciprocal space out to $2\theta = 130^\circ$ were surveyed; they numbered 1236, of which 49 had net intensities less than zero. Six reflections ($\bar{5}74$; $\bar{1}, 17, 1$; $\bar{1}, 17, 2$; $\bar{1}85$; $\bar{1}95$; and $\bar{1}, 10, 5$) were not recorded because of failures

* Contribution No. 4599 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109.

† Present address: Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138, U.S.A.